Thermal equation of state of copper studied by high *P-T* synchrotron x-ray diffraction

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The unit-cell volume of copper (Cu) has been measured by synchrotron x-ray at pressures and temperatures of up to 8.1 GPa and 1100 K. From pressure-volume-temperature (*P-V-T*) measurements, thermoelastic parameters of Cu were derived based on a modified high-*T* Birch–Murnaghan equation of state and a thermal pressure approach. The ambient bulk modulus derived from this work is comparable to previously reported value, whereas all other thermoelastic parameters of Cu have never been determined before. These results extend our knowledge of the fundamental thermophysical properties on Cu. © *2009 American Institute of Physics.*
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Copper, a ductile metal with excellent electrical and thermal conductivities, is one of the most important elements for both historical and contemporary uses. It has been utilized in a broad spectrum of applications, from coinage and household products to modern electronics. Copper stays in the same column of periodic table as silver and gold; each of them possesses one *s*-orbital electron on top of a full electron shell. This similarity in electronic configuration endows these metals with similar physical properties such as remarkable electrical conductivity. In addition, copper has many astonishing mechanical properties. For example, an extreme extensibility (elongation exceeding 5000%) has been observed in Cu.[1]

Though copper has been extensively studied theoretically and experimentally, most work has focused on its electronic properties and structural stability.[2–7] The high-pressure behavior is still poorly understood, and, to date, the thermoelastic equation of state (EOS) of copper has not been determined. The term of thermoelastic at most relates to the temperature dependent elastic features, such as temperature derivative of bulk modulus and pressure derivative of thermal expansion. All of these parameters are not only of great significance in understanding the overall properties of condensed matter but also in developing the theoretical modeling for correct computational simulations.

In the present work, we conduct simultaneous high-pressure and high-temperature experiments with high energy synchrotron x-ray diffraction to acquire the thermoelastic EOS for Cu. Thermal EOS parameters, such as bulk modulus, temperature derivative of the bulk modulus, volumetric thermal expansion, and the pressure derivative of thermal expansion, were derived by fitting the *P-V-T* data sets to a modified high-temperature Birch–Murnaghan EOS. A thermal pressure approach was also used to produce the temperature derivative of the bulk modulus at constant volume, a thermoelastic parameter that is experimentally difficult to measure.

At ambient conditions, Cu has a face-centered cubic structure with space group *Fm*3*m* (225). The starting Cu powders with grain sizes smaller than 10 μm were commercially obtained from Sigma–Aldrich. The high *P-T* experiments were conducted using a cubic anvil apparatus at beam line X17B2 of the National Synchrotron Light Source, Brookhaven National Laboratory. The white radiation from the superconducting wiggler magnet was used for energy-dispersive measurements. The diffracted x-rays were collected with a 13-element detector at a fixed Bragg angle of $2\theta = 6.4900°$. The cell assembly used in experiments has been described elsewhere.[8]

In the present study, NaCl was used as an internal pressure marker, and the sample pressure was calculated from Decker's EOS for NaCl.[9] The uncertainty in the pressure measurements is mainly due to the statistical variation in the positions of different diffraction peaks and is less than 0.2 GPa in the investigated *P-T* range. Temperatures were measured by a W/Re25%-W/Re3% thermocouple that was in direct contact with the sample. Diffraction patterns were obtained for the sample and NaCl in close proximity to the thermocouple junctions. Errors in the temperature measurements were estimated to be around 10 K.

The Cu sample was initially compressed at room temperature to a desired pressure, followed by heating to the maximum temperature of 1100 K and then stepwise cooling to 900, 700, 500, and 300 K. Similar run cycles were repeated several times at progressively higher pressures of up to ~8.1 GPa. To minimize deviatoric stress built up during the room-temperature "cold" compression using a solid pressure medium, all diffraction patterns in the experimental *P-T* space were collected after temperature reached 1100 K and during the subsequent cooling cycles. Our data analysis indicates that the peak widths observed under high *P-T* conditions are similar to those at ambient conditions, confirming that the present experiment was conducted near hydrostatic conditions. In addition, all the *P-V-T* data reported here were collected from a single high *P-T* experiment to eliminate the systematic errors, which are typically present among different measurements.

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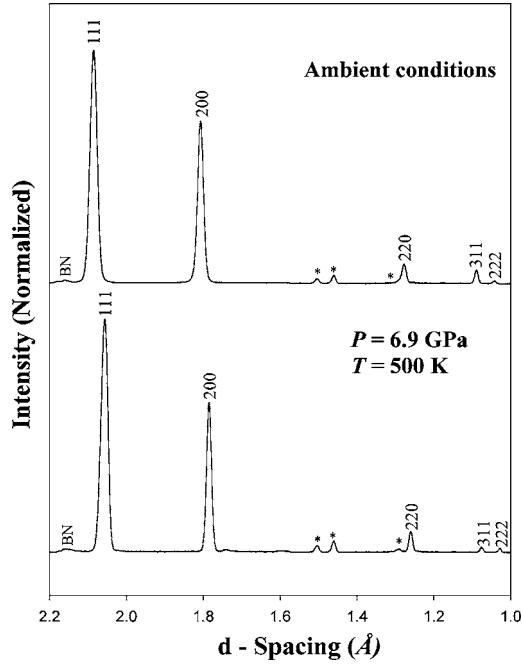b)Electronic mail: yzhao@lanl.gov.

FIG. 1. Representative x-ray diffraction patterns used for the determinations of unit-cell parameters of Cu under high *P-T* conditions. The peaks marked with stars are fluorescence lines of lead. The BN peaks come from the BN cylinder surrounding the sample.

Figure 1 shows x-ray diffraction patterns at selected *P-T* conditions. The lattice *d*-spacings were determined by Gaussian peak fitting of the diffracted intensity, and the unit-cell parameters were calculated by least-squares fitting based on a cubic unit cell using five diffraction lines. The relative standard deviations in determination of the unit-cell volumes, as plotted in Fig. 2 as a function of pressure and temperature, are typically less than 0.1%.

We employ a modified high-*T* Birch–Murnaghan EOS,[10–12] truncated to third order, to derive the thermoelastic parameters based on the measured *P-V-T* data for Cu. A general form of this modified EOS is

$$P = 3K_T f (1 + 2f)^{5/2} \left[1 - \tfrac{3}{2}(4 - K')f + \ldots \right], \qquad (1)$$

where

$$K_T = K_{To} + (\partial K/\partial T)(T - 300),$$

$$K' = \partial K/\partial P,$$

and

$$f = \tfrac{1}{2}\left[(V_T/V_{PT})^{2/3} - 1 \right],$$

$$V_T = V_0 \exp\left[\int \alpha(0,T)dT \right].$$

In Eq. (1), K_{To} and K_T represent the isothermal bulk modulus at 300 K and a higher temperature *T*, and $(\partial K/\partial T)$ and $(\partial K/\partial P)$ stand for the temperature and pressure derivatives of the bulk modulus, respectively. V_0, V_T, and V_{PT} correspond to the unit-cell volumes at ambient conditions, at atmospheric pressure and temperature *T*, and at high *P-T* conditions, respectively. $\alpha(0,T)$ is the volumetric thermal expansion at atmospheric pressure, commonly represented by $\alpha(0,T) = a + bT - c/T^2$ (*T* in Kelvin) (see Ref. 13). In the modified high-*T* Birch–Murnaghan EOS, the temperature ef-
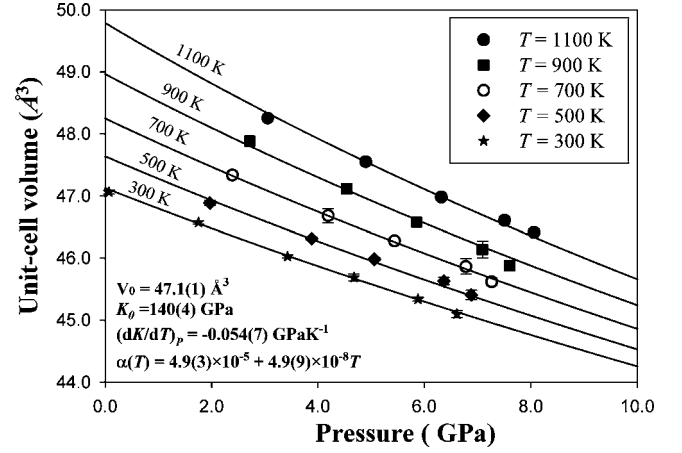

FIG. 2. The measured *P-V-T* data of Cu. The curves represent results of the least-squares fitting using Eq. (1). The ambient unit-cell volume (V_0) determined from the *P-V-T* fit is in good agreement with the reported value in Ref. 22.

fects are taken into account by replacing K_0 with K_T and substituting V_0/V_P with V_T/V_{PT} in the isothermal EOS. Because of the limited pressure coverage that restricts an accurate constraint on K' for Cu, we assume $K'=4$ in Eq. (1) throughout the data analysis. Similarly, we ignore the term of c/T^2 in $\alpha(0,T)$ as well as the higher-order terms and cross-derivatives of the bulk modulus such as $\partial^2 K/\partial T^2$ and $\partial^2 K/\partial P \partial T$. From a least-squares fit to all the *P-V-T* data using Eq. (1), we obtain $K_0 = 140(4)$ GPa, $(\partial K/\partial T)_P = -0.054(7)$ GPa K^{-1}, and $\alpha(0,T) = a + bT$ with $a = 4.9(3) \times 10^{-5}$ K^{-1} and $b = 4.9(9) \times 10^{-8}$ K^{-2}. Errors in the obtained thermoelastic parameters are those of the least-squares fitting. Uncertainties in the *P-V-T* measurements were not included in the error estimation. From the thermodynamic identity

$$(\partial \alpha/\partial P)_T = (\partial K/\partial T)_P K_{To}^{-2}, \qquad (2)$$

the pressure derivative of the volume thermal expansivity, $(\partial \alpha/\partial P)_T$, is thus calculated to be $-2.8 \pm 0.4 \times 10^{-6}$ K^{-1} GPa^{-1}. The uncertainty in $(\partial \alpha/\partial P)_T$ is estimated from the error propagation of K_0 and $(\partial K/\partial T)_P$.
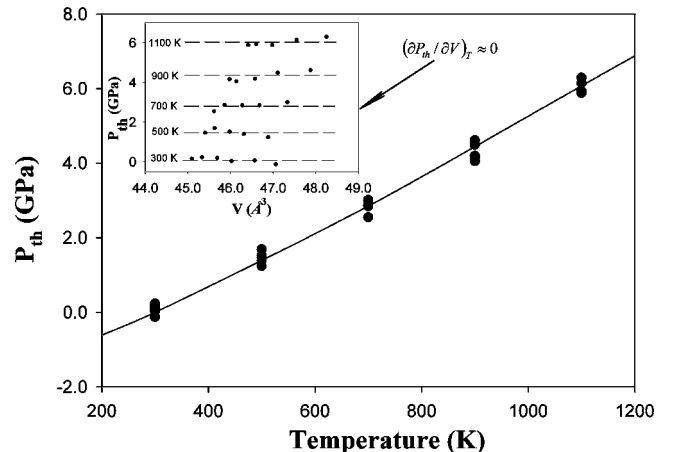

FIG. 3. Variation in the thermal pressure (P_{th}) of Cu as a function of temperature. The spread of the data points at any given temperature corresponds to thermal pressures at different volumes, which are plotted in detail in the inset. The dashed lines in the inset plot show approximate constant values of thermal pressure for a given temperature, indicating that thermal pressure is independent of the volume.

TABLE I. Summary of thermoelastic parameters for Cu. Except for $(\partial\alpha/\partial P)_T$, the numbers in parentheses are standard deviations from the least-squares fits and refer to the last digit of the parameter values. For $(\partial\alpha/\partial P)_T$, the uncertainties are estimated from the error propagation of K_0 and $(\partial K/\partial T)_P$.

| Reference | K_0 (GPa) | K_0' | $(\partial K/\partial T)_P$ (GPa K^{-1}) | $\alpha_T(\text{K}^{-1})=a+bT$ | | $(\partial\alpha/\partial P)_T$ (GPa K^{-1}), (10^{-6}) | $(\partial K/\partial T)_V$ (GPa K^{-1}) |
				a (10^{-5})	b (10^{-8})		
This work[a]	140(4)	4.0	−0.054(7)	4.9(3)	4.9(9)	−2.8 ± 0.4	
This work[b]	140(4)	4.0	−0.051(4)			−2.6 ± 0.3	−0.021(4)
[20]	137(0.9)						
[21]	137.4	5.52					

[a]Based on the measured *P-V-T* data and Eqs. (1) and (2).
[b]Thermal pressure approach based on the measured data and Eqs. (3) and (4).

The thermal pressure approach has been widely applied in processing *P-V-T* data, as it can provide important thermodynamic insights.[12,14–17] This method is also useful for deriving the thermoelastic parameter $(\partial K_T/\partial T)_V$, the temperature derivative of bulk modulus at constant volume, which is experimentally difficult to measure. In this approach, thermal pressure P_{th} is calculated as the difference between the measured pressure at a given temperature and the calculated pressure from Eq. (1) at room temperature, with both pressures corresponding to the same volume. Following this definition, thermal pressures were calculated for Cu and are plotted in Fig. 3. An inspection of Fig. 3 demonstrates that thermal pressure varies linearly with temperature, which is consistent with the linear trend revealed in many different classes of condensed matter.[14–19] Thermal pressure at any temperature above 300 K for a given volume can also be analyzed from thermodynamic relations. Following the method of Anderson[14,15] and his subsequent studies, thermal pressures of Cu were calculated by

$$P_{\text{th}} = \int_{300}^{T} (\partial P/\partial T)_V \, dT$$
$$= P_{\text{th}}(V,T) - P_{\text{th}}(V,300)$$
$$= \left[\alpha K_T(V_{300},T) + (\partial K_T/\partial T)_V \ln(V_{300}/V)\right](T-300). \tag{3}$$

From the least-squares fit of the thermal pressure versus temperature shown in Fig. 3, we obtain average values of $\alpha K_T(V_{300},T)$ and $(\partial K_T/\partial T)_V$ that are 0.0075(1) and −0.021(4) GPa K^{-1}, respectively. From the thermodynamic identity

$$(\partial K_T/\partial T)_V = (\partial K_T/\partial T)_P + (\partial K_T/\partial P)_T \alpha K_T(V_{300},T), \tag{4}$$

we obtain a value of −0.051(4) for $(\partial K_T/\partial T)_P$, which is in agreement with the results derived from Eq. (1). The value of $(\partial\alpha/\partial P)_T$ derived from Eq. (2) is $-2.6\pm0.3 \times 10^{-6}$ K^{-1} GPa^{-1}. Internally consistent thermal EOSs for Cu, as summarized in Table I, are thus obtained using different analysis methods. Within the experimental uncertainties, the K_0 value we obtained is in good agreement with those previously determined by the ultrasonic approach (see Table I) and x-ray diffraction in a diamond cell (see Table I), whereas the thermoelastic parameters $(\partial K/\partial T)_P$, $(\partial K/\partial T)_V$, and $(\partial\alpha/\partial P)_T$, were never determined before.

In conclusion, we have conducted *in situ* x-ray diffraction experiments for Cu at pressures of up to 8.1 GPa and temperatures of up to 1100 K. From these measurements a complete thermal EOS of Cu has been derived. Two different methods, namely, high-*T* EOS and thermal pressure, have been applied in the data analysis. The overall thermoelastic parameters, including temperature and pressure derivatives of thermal expansion and elastic bulk modulus, are internally consistent with the two different approaches. Within the experimental uncertainty, the bulk modulus obtained in our study is in good agreement with the value determined previously with acoustic-resonance spectroscopy.

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